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Novel Lanthanocene Analogues of “Carbons Apart” Erba- and Dysprosacarboranes: Synthetic and Structural Investigation

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*Summary: The reaction of closo-exo-5,6-Na(THF)$_2$-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (**1**) and anhydrous LnCl$_3$, in a molar ratio of 3:1, in dry benzene at 60 °C produced novel lanthanocene analogues of metallacarborane complexes of the formula [Na$_3$][1,1′-[5,6-(μ-H)$_2$-nido-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-commo-Ln-(2,4-C$_2$B$_4$H$_4$)$_2$] (Ln = Er (**2**), Dy (**3**)) as yellow crystalline solids in 82% and 78% yields, respectively, thus establishing a new structural pattern for lanthanacarboranes.*

The chemistry of lanthanide complexes of the C_2B_{10} and C_2B_9 carborane ligand systems began in 1988 with the first report of the synthesis and structural characterization of [3,3′-(THF)$_2$-*commo*-3,3′-Sm($C_2B_9H_{11}$)$_2$]$^-$ by Hawthorne and co-workers.[1] Soon after the first report in 1991 of the yttracarborane sandwich complex,[2] Hosmane et al. demonstrated that the reactivities of the small-cage carborane ligands toward lanthanide reagents are distinctly different from those of the large-cage C_2B_9 and C_2B_{10} carborane systems.[3] Subsequently, a number of icosahedral and supraicosahedral carborane sandwich and half-sandwich complexes of the lanthanacarboranes have been described.[4−6] Our results have shown that the reaction of the THF-solvated dilithium compound of the [2,3-(SiMe$_3$)$_2$C$_2$B$_4$H$_4$]$^{2-}$ dianion with anhydrous LnCl$_3$ in a molar ratio of 2:1 in dry benzene and THF produced unusual trinuclear Ln(III) carboranes of the form {[η^5-1-Ln-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$-[(μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$(μ_3-OMe)]-[μ_2-Li(THF)]$_3$-(μ_3-O)},[3a−e,h,l] indicating the initial formation of a half-sandwich lanthanacarborane which then reacts with the remaining lithiacarborane precursors in the presence of degraded fragments of the THF solvent to yield the corresponding trinuclear Ln(III) cluster.[3a−e,h,l] The recent report on the synthesis and crystal structure of the monomeric half-sandwich samaracarborane {1,1-(*t*-C$_4$H$_9$-OH)$_2$-1-(*t*-C$_4$H$_9$O)-2,3-(SiMe$_3$)$_2$-4,5-[Li(THF)Cl]-*closo*-η^5-1-Sm-2,3-C$_2$B$_4$H$_4$}·THF[3k] lends support to the proposed sequence of reactions. However, when TMEDA was substituted for THF, the courses of the reactions were quite different in that full-sandwich dichlorolanthanacarboranes were the only discernible products.[3f,i,j] Although these reports unambiguously showed the influence of the coordinating solvents in the formation of lanthanacarboranes, they gave no indication of forming lanthanocene analogues in which the central lanthanide metal is complexed to each of the three open five-membered bonding faces in an η^5 fashion.[7] Here we report the synthesis and crystal structure of the unprecedented erba- and dysprosacarborane complexes

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(1) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458−4459.

(2) (a) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Organometallics* **1991**, *10*, 3964−3966. (b) Hosmane, N. S.; Zhu, D.; Zhang, H.; Oki, A. R.; Maguire, J. A. *Organometallics* **1998**, *17*, 3196−3203.

(3) (a) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 432−434. (b) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081−1124. (c) Hosmane, N. S.; Maguire, J. A. *J. Cluster Sci.* **1993**, *4*, 297−349. (d) Hosmane, N. S.; Wang, Y.; Oki, A. R.; Zhang, H.; Zhu, D.; McDonald, E. M.; Maguire, J. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *93−94*, 253−256. (e) Zhang, H.; Oki, A. R.; Wang, Y.; Maguire, J. A.; Hosmane, N. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *C51*, 635−638. (f) Hosmane, N. S.; Wang, Y.; Zhang, H.; Oki, A. R.; Maguire, J. A.; Waldhör, E.; Kaim, W.; Binder, H.; Kremer, R. K. *Organometallics* **1995**, *14*, 1101−1103. (g) Zhang, H.; Wang, Y.; Maguire, J. A.; Hosmane, N. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *C52*, 8−11. (h) Hosmane, N. S.; Wang, Y.; Oki, A. R.; Zhang, H.; Maguire, J. A. *Organometallics* **1996**, *15*, 626−638. (i) Hosmane, N. S.; Wang, Y.; Zhang, H.; Maguire, J. A.; McInnis, M.; Gray, T. G.; Collins, J. D.; Kremer, R. K.; Binder, H.; Waldhör, E.; Kaim, W. *Organometallics* **1996**, *15*, 1006−1013. (j) Zhang, H.; Wang, Y.; Maguire, J. A.; Hosmane, N. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *C52*, 640−643. (k) Hosmane, N. S.; Oki, A. R.; Zhang, H. *Inorg. Chem. Commun.* **1998**, *1*, 101−104. (l) Zheng, C.; Hosmane, N. S.; Zhang, H.; Zhu, D.; Maguire, J. A. *Internet J. Chem.* **1999**, *2*, 10 (URL: http://www.ijc.com/articles/1999v2/10/). (m) Hosmane, N. S.; Li, S.-J.; Zheng, C.; Maguire, J. A. *Inorg. Chem. Commun.* **2001**, *4*, 104−107. (n) Hosmane, N. S.; Wang, Y.; Zhang, H.; Zhu, Y.; Maguire, J. A. *Inorg. Chem. Commun.* **2001**, *4*, 547−550.

(4) (a) Khattar, R.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 1970−1972. (b) Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009−2017. (c) Khattar, R.; Manning, M. J.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chem.* **1992**, *31*, 268−273.

(5) (a) Xie, Z.; Liu, Z.; Chiu, K.-Y.; Xue, F.; Mak, T. C. W. *Organometallics* **1997**, *16*, 2460−2464. (b) Xie, Z.; Liu, Z.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3603−3609. (c) Xie, Z.; Wang, S.; Zhou, Z.; Xue, F.; Mak, T. C. W. *Organometallics* **1998**, *17*, 489−491. (d) Xie, Z.; Wang, S.; Zhou, Z.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907−1909. (e) Xie, Z.; Wang, S.; Zhou, Z.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641−1652. (f) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 2420−2427. (g) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 4478−4487. (h) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3947−3949. (i) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 334−343. (j) Chui, K.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 1391−1401. (k) Chiu, K.; Zhang, Z.; Mak, T. C. W.; Xie, Z. *J. Organomet. Chem.* **2000**, *614−615*, 107−112.

(6) (a) Shaw, K. F.; Reid, B. D.; Welch, A. J. *J. Organomet. Chem.* **1994**, *482*, 207−220. (b) Lebedev, V. N.; Shemyakin, N. F.; Soldovnikov, S. P.; Zakharkin, L. I. *Metalloorg. Khim.* **1988**, *1*, 718−718.

(7) Edelmann, F. T. In *Comprehensive Organometallic Chemistry-II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 4, Chapter 2, pp 11−212.

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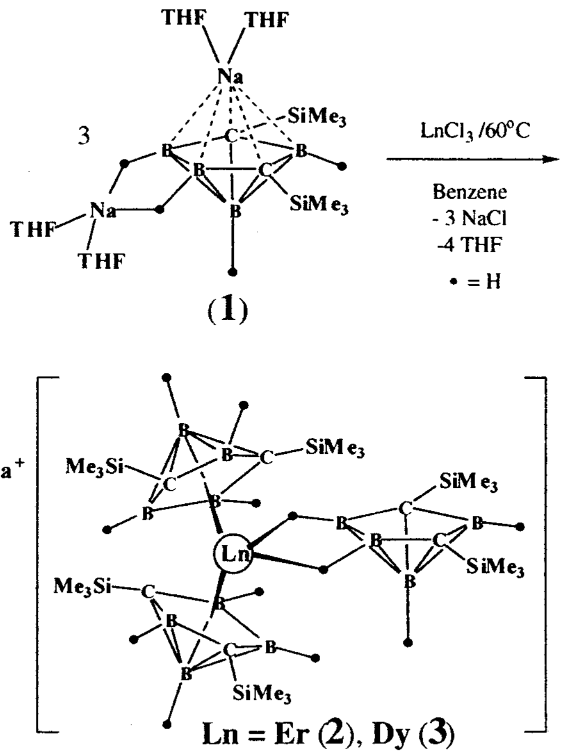
Scheme 1. Synthesis of Erba- and Dysprosacarborane Complexes



whose geometry around the central metal atom somewhat resembles that of lanthanocene analogues.

The reaction between *closo*-*exo*-5,6-$\mathrm{Na(THF)_2}$-1-$\mathrm{Na(THF)_2}$-2,4-$\mathrm{(SiMe_3)_2}$-2,4-$\mathrm{C_2B_4H_4}$ (**1**) and anhydrous $\mathrm{LnCl_3}$, in a molar ratio of 3:1, in dry benzene at 60 °C produced, in 82% and 78% yields, novel lanthanacarborane complexes of the formula $\mathrm{[Na_3]}$[1,1′-[5,6-(μ-H)$_2$-*nido*-2,4-$\mathrm{(SiMe_3)_2}$-2,4-$\mathrm{C_2B_4H_4}$]-2,2′,4,4′-$\mathrm{(SiMe_3)_4}$-1,1′-*commo*-Ln(2,4-$\mathrm{C_2B_4H_4}$)$_2$] (Ln = Er (**2**), Dy = (**3**)) as yellow crystalline solids (Scheme 1).[8] The most important observation is the absence of any solvent coordination to the central metal atom in both **2** and **3**, unlike most of the lanthanacarboranes known to date.[1–6] This is presumably due to the higher reaction temperature of 60 °C in dry benzene, rather than the usual reaction temperature of 0−25 °C, that restricts the coordination of the liberated THF, from the Na atom in the precursor, to bond to the central metal atom. This is a significant advance in synthetic lanthanacarborane chemistry.

Due to the paramagnetic nature of **2** and **3**, the NMR spectra did not prove useful in the elucidation of their geometries. The solution IR spectra of **2** and **3** exhibit well-resolved terminal B−H stretches.[9] Such fine structures of B−H stretching bands have been previously observed in other *closo*- and *commo*-lanthanacarboranes and has been explained on the basis of unequal interactions of the boron-bound hydrogens with metal groups present in the complex.[3h,i,k,4] The unambiguous structure of the title compound was determined by X-ray diffraction studies.[10]

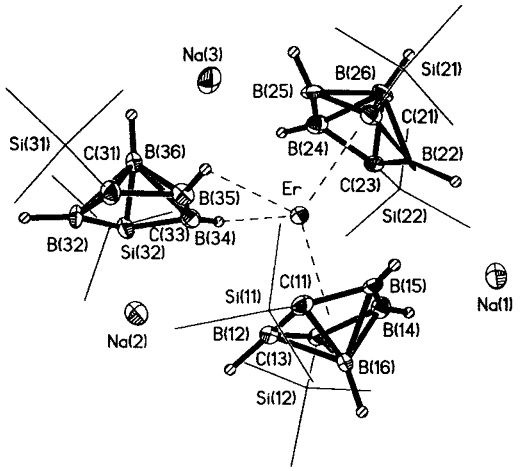


Figure 1. Perspective view of **2** drawn at the 50% probability level. Pertinent distances (Å) and angles (deg): Er−($\mathrm{C_2B_3}$ centroid 1,2) = 2.324, 2.305; Er−C(11,13,21,23) = 2.642(8), 2.708(8), 2.706(8), 2.650(8); Er−B(12,14,15,22,24,25,34,35) = 2.704(9), 2.673(9), 2.620(9), 2.703(8), 2.668(9), 2.696(9), 2.608(10), 2.632(10); (centroid 1)−Er−(centroid 2) = 130.9 (see the Supporting Information for a detailed list of bond lengths and angles). The *n*-hexane and benzene molecules of crystallization and all of the exo-polyhedral $\mathrm{SiMe_3}$ units are omitted for clarity.

The X-ray crystal structures of **2** and **3** (see Figures 1 and 2)[10] show that both the complexes are isostructural with the presence of two molecules of lanthanacarborane, each associating with one *n*-hexane and 1.5 benzene molecules of crystallization in the unit cell. The lanthanide metal in each complex is η^5-bonded to two "carbons apart" $\mathrm{C_2B_4}$ carborane cages with the additional bonding to the third $\mathrm{C_2B_4}$ cage in an η^2 fashion using two of the adjacent B−H$_{\mathrm{terminal}}$ bonds. Although the $\mathrm{C_2B_3}$ bonding face of the third carborane cage is not

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(8) **Synthesis of 2 and 3.** A 3.19 mmol (1.76 g) sample of *closo*-*exo*-5,6-$\mathrm{Na(THF)_2}$-1-$\mathrm{Na(THF)_2}$-2,4-$\mathrm{(SiMe_3)_2}$-2,4-$\mathrm{C_2B_4H_4}$ (**1**) (Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Onak, T. P. *Inorg. Chem.* **1991**, *30*, 3793−3795) was reacted with 1.06 mmol of anhydrous $\mathrm{ErCl_3}$ (0.290 g) or $\mathrm{DyCl_3}$ (0.285 g) in dry benzene (10 mL) at 60 °C for 24 h, during which time the solution turned yellow and turbid. The heterogeneous product mixture was then filtered in vacuo and the solvent removed from the filtrate to collect a pale yellow solid. This solid was extracted in benzene and then filtered again to collect a clear yellow solution. Removal of the solvent from this clear solution gave a yellow solid that was later recrystallized from dry *n*-hexane to collect air-sensitive crystals, identified as $\mathrm{[Na_3]}$[1,1′-[5, 6-(μ-H)$_2$-*nido*-2,4-$\mathrm{(SiMe_3)_2}$-2,4-$\mathrm{C_2B_4H_4}$]-2,2′,4,4′-$\mathrm{(SiMe_3)_4}$-1,1′-*commo*-Ln(2,4-$\mathrm{C_2B_4H_4}$)$_2$], in yields of 82% (Ln = Er (**2**); 0.84 g, 0.87 mmol; mp >250 °C dec) and 78% (Ln = Dy (**3**); 0.80 g, 0.83 mmol; mp >250 °C dec). Both **2** and **3** are soluble in polar solvents and slightly soluble in *n*-hexane. The X-ray-quality crystals were grown separately from a solution mixture of *n*-hexane (10%) and benzene (90%) and subsequently used in X-ray analyses.

(9) **IR and Analytical Data.** IR (KBr pellet, cm^{-1}): **2**, 2512 (s, s), 2468 (s, br), 2434 (br, sh), 2353 (s, s), 2236 (s, br), 2282 (s, s) [ν(B−H)]; **3**, 2506 (s, s), 2467 (s, br), 2432 (br, sh), 2360 (s, s), 2283 (s, s) [ν(B−H)]. Anal. Calcd for $\mathrm{C_{24}H_{66}B_{12}Si_6Na_3Er\cdot C_6H_6}$ (**2**): C, 37.25; H, 7.50. Found: C, 37.78; H, 7.68. Calcd for $\mathrm{[C_{24}H_{66}B_{12}Si_6Na_3Dy\cdot C_6H_6]_3\cdot 2C_6H_{14}}$ (**3**): C, 40.04; H, 8.03. Found: C, 40.37; H, 7.80.

(10) X-ray data for **2** ($\mathrm{C_{39}H_{89}B_{12}Si_6ErNa_3}$; fw 1092.59; *P*2$_1$/*n*) and **3** ($\mathrm{C_{39}H_{89}B_{12}Si_6DyNa_3}$; fw 1087.83; *P*2$_1$/*n*) are as follows. Data were collected at 173(2) K on a Bruker SMART CCD PLATFORM diffractometer with a = 11.978(3) and 11.980(3) Å, b = 19.115(4) and 19.160(5) Å, c = 26.350(6) and 26.411(7) Å, β = 92.035(4) and 91.890(5)°, V = 6029(2) and 6059(3) Å^3, Z = 4 and 4, and D_{calcd} = 1.204 and 1.193 Mg/m^3 for **2** and **3**, respectively. Of the 28891 and 29042 reflections collected (2θ = 3.68−50° for **2** and 2.62−50° for **3**), 10367 and 10539 reflections were respectively considered as observed ($I > 2\sigma(I)$) and were corrected for Lorentz, polarization, and absorption effects (Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Göttingen, Germany, 1996). The structures were solved by direct methods and refined by full-matrix least-squares techniques using SHELXTL (Sheldrick, G. M. SHELXTL, Version 5.1; Bruker Analytical X-ray Systems, Madison, WI, 1997). All non-H atoms were refined anisotropically. The final refinements converged at R1 = 0.0770 and 0.0596, wR2 = 0.1594 and 0.1225, and GOF = 1.561 and 1.490 for **2** and **3**, respectively.

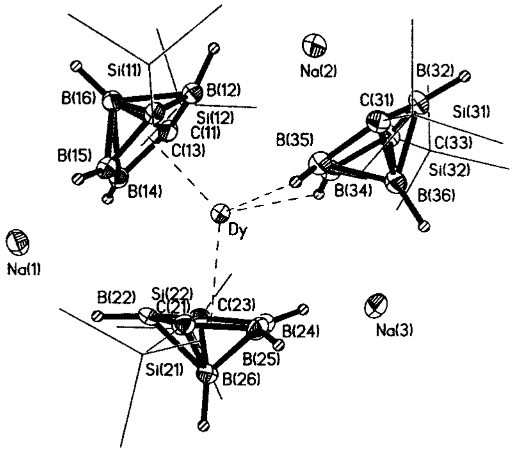

Figure 2. Perspective view of **3** drawn at the 50% probability level. Pertinent distances (Å) and angles (deg): Dy−(C_2B_3 centroid 1,2) = 2.336, 2.342; Dy−C(11,13,21,23) = 2.669(6), 2.741(6), 2.727(6), 2.673(6); Dy−B(12,14,15,22,24,25,34,35) = 2.721(7), 2.698(7), 2.654(7), 2.719(6), 2.686(7), 2.723(7), 2.650(7), 2.665(7); (centroid 1)−Dy−(centroid 2) = 131.0 (see the Supporting Information for a detailed list of bond lengths and angles). The *n*-hexane and benzene molecules of crystallization and all of the exo-polyhedral $SiMe_3$ units are omitted for clarity.

complexed, the presence of this cage in the vicinity of the central lanthanide metal is significant in that the metal bonds only to the carborane ligands, as evident in these structures. It is important to note that the solid-state structures of monomeric [η^5-1,3-$(Me_3Si)_2C_5H_3]_3Ln$ (Cp''_3Ln; Ln = Sm, La, Nd, Gd, Dy) have been reported.[11,12] Since the two "nonadjacent" cage carbons carry large $SiMe_3$ groups on the five-membered bonding face, as in the Cp″ ligand system, it is surprising that the full complexation of the third carborane bonding face to the same lanthanide metal was not possible. Consequently, the Cent(1)−Ln−Cent(2) angles of 130.9 and 131.0° in **2** and **3** are significantly larger than the equivalent angles of 117.5, 117.7, and 120.0 ± 1° found in the structures of (η^5-$C_5H_5)_3Er(THF)$,[13] (η^5-$C_5H_5)_3Dy(THF)$,[14] and [η^5-1,3-$(Me_3Si)_2C_5H_3]_3Ln$ (Ln = Sm, La, Nd, Gd, Dy),[11,12] respectively. However, the solid-state structures of the unsubstituted tris(cyclopentadienyl)-lanthanides do not consist of isolated $Ln(Cp)_3$ molecules, due to their strong tendency to adopt high coordination numbers; therefore, they form oligomers or polymeric chains.[7] The two metal−C_2B_3(centroid) distances of 2.324 and 2.305 Å in **2** and of 2.336 and 2.342 Å in **3** along with the two Ln−B distances (2.608(10) and 2.632(10) Å in **2** and 2.650(7) and 2.665(7) Å in **3**) to the third carborane cage give a very distorted tetrahedral arrangement about the lanthanide metal (see Figures 1 and 2).[10] Since carborane ligands carry a 2− charge, for charge compensation three uncomplexed Na^+ ions are present in each molecule without influencing the cage geometries.

The absence of the coordinating solvent, THF, either on the lanthanide metal or the spectator ions indicates that a detailed investigation of the novel reactivity and structural patterns in lanthanacarborane chemistry of this kind is therefore warranted. Such an investigation is currently underway in our laboratories.

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Supporting Information Available: Tables of crystallographic data for compounds **2** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *J. Organomet. Chem.* **1990**, *394*, 87−97.

(12) Xie, Z.; Chui, K.; Liu, Z.; Xue, F.; Zhang, Z.; Mak, T. C. W.; Sun, J. *J. Organomet. Chem.* **1997**, *549*, 239−244.

(13) Chen, W.; Lin, G.; Xia, J.; Wei, G.; Zhang, Y.; Jin, Z. *J. Organomet. Chem.* **1994**, *467*, 75−78.

(14) Ye, Z.; Wang, S.; Yu, Y. *Inorg. Chim. Acta* **1990**, *177*, 97−100.